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NASA Technical Paper 3064

March 1991

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NASA

NASA
Technical
Paper
3064

1991

Investigation of Microstructural Changes in Polyetherether-Ketone Films at Cryogenic Temperatures by Positron Lifetime Spectroscopy

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Abstract

Microstructural changes in polyetherether-ketone (PEEK) films have been investigated in the temperature range of 23°C to −196°C by using positron lifetime spectroscopy. It has been determined that the total free volume decreases by about 46 percent in amorphous PEEK samples and about 36 percent in semicrystalline PEEK samples when they are cooled from room temperature to the temperature of liquid nitrogen. If this trend in reduction of free volume with decreasing temperature continues, as expected, PEEK should be able to withstand cooling to the temperature of liquid hydrogen without any detrimental effect on its diffusivity for liquid hydrogen.

Introduction

Polyetherether-ketone (PEEK) is a high-temperature thermoplastic polymer with excellent properties for a wide range of demanding applications. When heated above its melting temperature T_m and then rapidly quenched to ambient or lower temperatures, the polymer can be isolated in its amorphous form, which has a glass transition temperature T_g of 143°C. Once the amorphous form of the material is exposed to a temperature between T_g and T_m, it rapidly transforms to a semicrystalline form, which has a greatly suppressed glass transition temperature. The chemical structure of PEEK is shown in figure 1.

Polyetherether-ketone is a strong candidate for the matrix of the fiber-reinforced composites under consideration for the slush hydrogen fuel tank for the National Aero-Space Plane (NASP). However, there is some concern that PEEK might undergo molecular rearrangements under cryogenic conditions which may result in fuel leakage. Positron lifetime spectroscopy (PLS) has been used to investigate morphological features of PEEK as a function of temperature in the range of 77K to 300K, and the results of these measurements are described herein.

Symbols

A bar over a symbol indicates an average value.

C	microstructural constant
F	$= f_2 + f_3$
f_2, f_3	free-volume fractions associated with second and third lifetime components
I_1, I_2, I_3	intensities of first, second, and third lifetime components
LN_2	liquid nitrogen
PEEK	polyetherether-ketone
T_g	glass transition temperature, °C
T_m	melting temperature, °C
V_{f2}, V_{f3}	free-volume cell size for second and third lifetime components
τ_1, τ_2, τ_3	lifetimes of first, second, and third components

Experimental Procedure

Ten-mil-thick PEEK films were obtained from ICI Films, a business subsidiary of ICI Americas, Inc. The as-received films were unoriented, noncrystalline, and transparent. The semicrystalline variety of these films was prepared by heating them to 160°C for 1 hour and allowing them to cool to room temperature. The presence of crystallinity was evidenced by the onset of opacity in the films.

The Na^{22} positron lifetimes in the test films were measured in order to infer the concentration and size distributions of free-volume cells in them. (See refs. 1 and 2.) Since the single-film thickness (0.25 mm thick) was inadequate to stop the majority of Na^{22} positrons, the films were folded three times to make test coupons that were 0.75 mm thick, 2.5 cm long, and 2.5 cm wide. The Na^{22} source foil was sandwiched between two test coupons, and positron lifetime spectra in them were measured by using the standard fast-fast coincidence measurement technique (ref. 3). However, before starting extensive lifetime measurements in the test coupons, spectra were also measured in single 0.25-mm-thick films by using a recently developed (refs. 4 and 5) slow positron beam generator. These spectra were then compared with the lifetime spectra in the 0.75-mm-thick coupons. The results are summarized in table I. It is obvious that the results are in very good agreement. This indicates that the three films in the test coupons are in intimate contact with each other. (Or, at least, the annihilation lifetimes in the noncontact islands (free-volume cells) at the interface are outside the experimental time window of 50 nsec.) After this test, all measurements were made with three-fold test coupons in standard PLS geometry for thick targets, since this arrangement permits easier sample temperature control.

Positron lifetime measurements in both the amorphous and semicrystalline PEEK test coupons were made at a series of decreasing temperatures, beginning with the ambient temperature.

Amorphous Films

The PLS measurements in as-received PEEK film samples were made at a steady-state temperature of

23°C (room temperature), −12°C, −40°C, −62°C, and −196°C. The −12°C and −40°C measurements were made by using the system illustrated in figure 2, while the −62°C and −196°C measurements were made with the system illustrated in figure 3. The results in amorphous films are summarized in table II.

Semicrystalline Films

The semicrystalline films were prepared by heating the amorphous films to 160°C and then allowing them to cool to room temperature. No attempt was made to release any thermal stress that may have been induced in the test samples to better simulate real service conditions. Lifetime measurements were made at room temperature before heating the films to 160°C and after cooling them to room temperature. Following room-temperature measurements, lifetime measurements were made at the same temperatures as amorphous films. These results are summarized in table III.

On the basis of lifetime data, the free-volume fraction (ref. 6) associated with microvoids in the PEEK samples has been calculated. The results are summarized in table IV. It is obvious that the total free-volume fraction decreases with decreasing temperature in both phases of the PEEK samples.

Results and Discussion

The microstructures of the two phases, as well as the effects of temperature on them, are different. For example, the sizes of the two amorphous sample microvoid population groups average about 9.9×10^{-3} nm^3 and 8.3×10^{-2} nm^3 at room temperature, whereas the corresponding sizes in the semicrystalline samples are 1.7×10^{-3} nm^3 and 8.8×10^{-2} nm^3. As the sample temperature is lowered from room temperature (23°C) to LN_2 temperature (−196°C), the smaller hole size increases from 9.9×10^{-3} nm^3 to 1.2×10^{-2} nm^3 in the amorphous sample, and it goes from 1.7×10^{-3} nm^3 to 8.9×10^{-3} nm^3 in the semicrystalline sample. The larger microvoids remain unchanged in size with decreasing temperature in both phases, though their concentrations are drastically reduced. The total free volume associated with both groups of microvoids in both types of samples of PEEK has been calculated. It goes down from 0.50 percent to 0.26 percent in the amorphous samples and from 0.44 percent to 0.28 percent in the semicrystalline samples as the sample temperatures are lowered from room temperature to LN_2 temperature. These results are illustrated in figures 4 to 9.

Several interesting conclusions can be drawn from these figures: (1) The concentration of both types of microvoids decreases with decreasing temperature in both phases of PEEK; (2) The free-volume fraction associated with larger microvoids decreases, and the fraction associated with smaller microvoids increases, as the sample temperature is lowered; (3) There is a net decrease in total free-volume fraction with decreasing temperature in both phases of PEEK. The last two conclusions indicate that some of the larger microvoids disappear altogether, whereas a smaller fraction of them reappear as intermediate-sized microvoids.

From the preceding discussion, it appears that PEEK undergoes conformational changes when its temperature is lowered. However, these conformational changes appear to reduce the free-volume fraction in the material and therefore make it less likely to suffer deleterious effects on its diffusivity for hydrogen when cooling to LH_2 temperature.

Concluding Remarks

The morphology of amorphous and semicrystalline polyetherether-ketone (PEEK) samples has been investigated at a number of temperatures in the range of 23°C to −196°C. Free-volume fraction in PEEK decreases as its temperature is lowered to that of liquid nitrogen (LN_2). Consequently, PEEK should not suffer any adverse effects on its diffusivity for hydrogen when exposed to LH_2 temperature if, as expected, the trend in reduction in free volume with decreasing temperature continues.

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February 7, 1991

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Table I. Comparison of Lifetime Data in Single and Three-Fold PEEK Films at Room Temperature

Single-layer film; positron beam measurement			Triple-layer film; conventional lifetime measurement		
τ_1/I_1, psec/percent	τ_2/I_2, psec/percent	τ_3/I_3, psec/percent	τ_1/I_1, psec/percent	τ_2/I_2, psec/percent	τ_3/I_3, psec/percent
274±6/52±2	561±23/25±3	1841±21/23±2	268±8/51±1	569±19/26±2	1823±27/23±2

Table II. Summary of Results in Amorphous PEEK at Various Temperatures

Temperature[a], °C	τ_1/I_1, psec/percent	τ_2/I_2, psec/percent	τ_3/I_3[b], psec/percent
23	278±11/53±3	589±39/25±2	1854±30/22±2
−12	312±8/68±2	825±32/17±2	1854±30/15±1
−40	344±9/76±2	858±25/10±2	1854±30/14±1
−62	381±8/75±2	850±40/10±2	1854±30/15±1
−196	334±8/79±2	879±38/11±2	1854±30/10±1

[a]Temperature errors are ≤1°C.

[b]Ortho-positronium lifetime has been held constant at room-temperature average value of 1854±30 psec, since its value at different temperatures changes by less than experimental error.

Table III. Summary of Results in Semicrystalline PEEK at Various Temperatures

Temperature[a], °C	τ_1/I_1, psec/percent	τ_2/I_2, psec/percent	τ_3/I_3[b], psec/percent
23	290±5/57±2	616±22/25±2	1914±19/18±1
−14	275±9/65±2	596±33/21±2	1914±19/14±1
−35	310±12/67±2	643±38/20±2	1914±19/13±1
−60	316±10/70±2	675±38/17±2	1914±19/13±1
−196	328±9/77±2	803±28/13±2	1914±19/10±1

[a]Temperature errors are ≤1°C.

[b]Ortho-positronium lifetime has been held constant at room-temperature average value of 1914±19 psec, since its value at different temperatures changes by less than experimental error.

Table IV. Comparison of Microvoid Sizes of Amorphous and Semicrystalline Samples of PEEK at Various Temperatures

[Errors in f_2, f_3, and F are $\leq$5 percent]

Temperature, °C	Small microvoids		Large microvoids		Total free volume[c], F, percent
	τ_2/I_2, psec/percent	f_2[a], percent	τ_3/I_3, psec/percent	f_3[b], percent	
Amorphous sample					
23	589/25	0.01	1854/22	0.49	0.50
−12	825/17	.04	1854/15	.35	.39
−40	858/10	.04	1854/14	.33	.37
−62	850/10	.03	1854/15	.34	.37
−196	879/11	.04	1854/10	.23	.27
Semicrystalline sample					
23	616/25	0.01	1914/18	0.43	0.44
−14	596/21	.01	1914/14	.34	.35
−35	643/20	.01	1914/13	.32	.33
−60	675/17	.02	1914/13	.32	.34
−196	803/13	.04	1914/10	.24	.28

[a]Free-volume fraction $f_2 = CI_2V_{f2}$

[b]Free-volume fraction $f_3 = CI_3V_{f3}$

[c]The constant C has been obtained by equating $F = f_2 + f_3$ to the reported value of saturation moisture pickup in PEEK (amorphous).

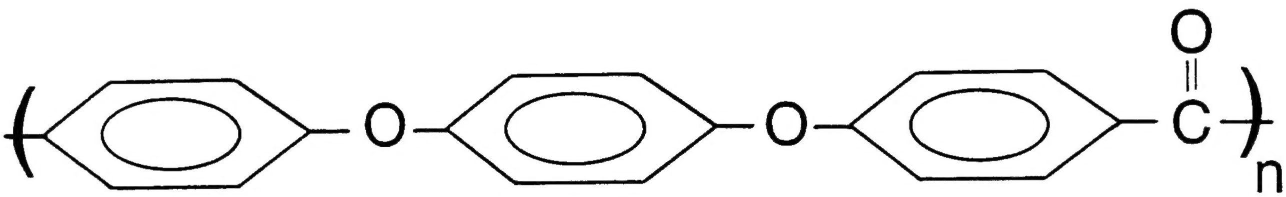

Figure 1. Chemical structure of PEEK.

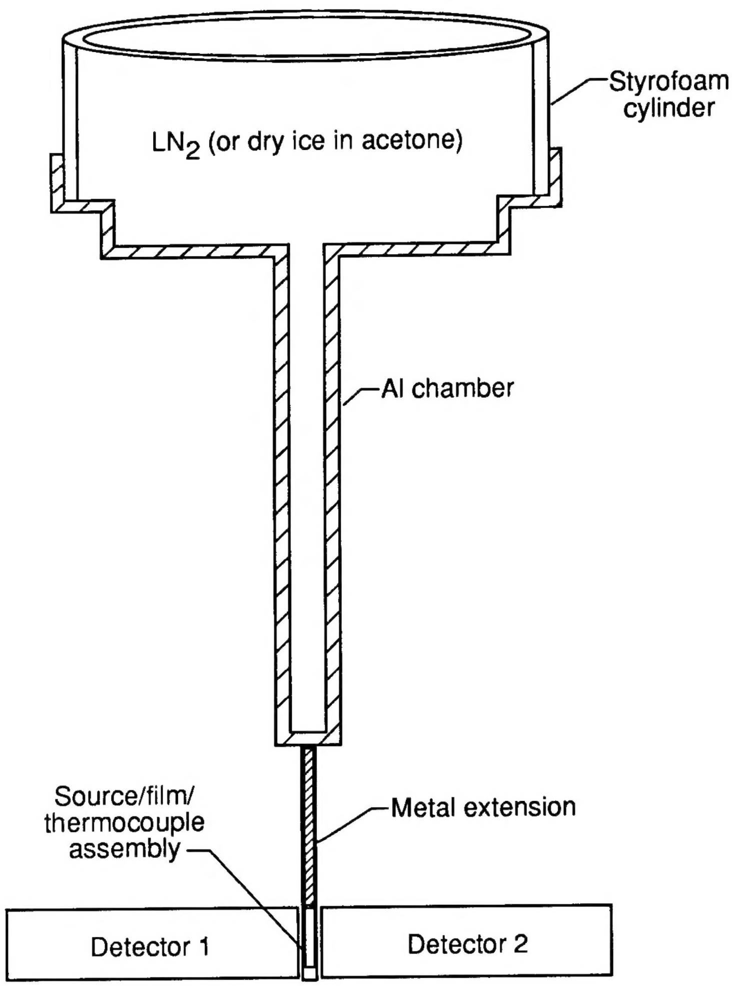

Figure 2. Schematic diagram of sample assembly for lifetime measurements at $-12°C$ and $-40°C$.

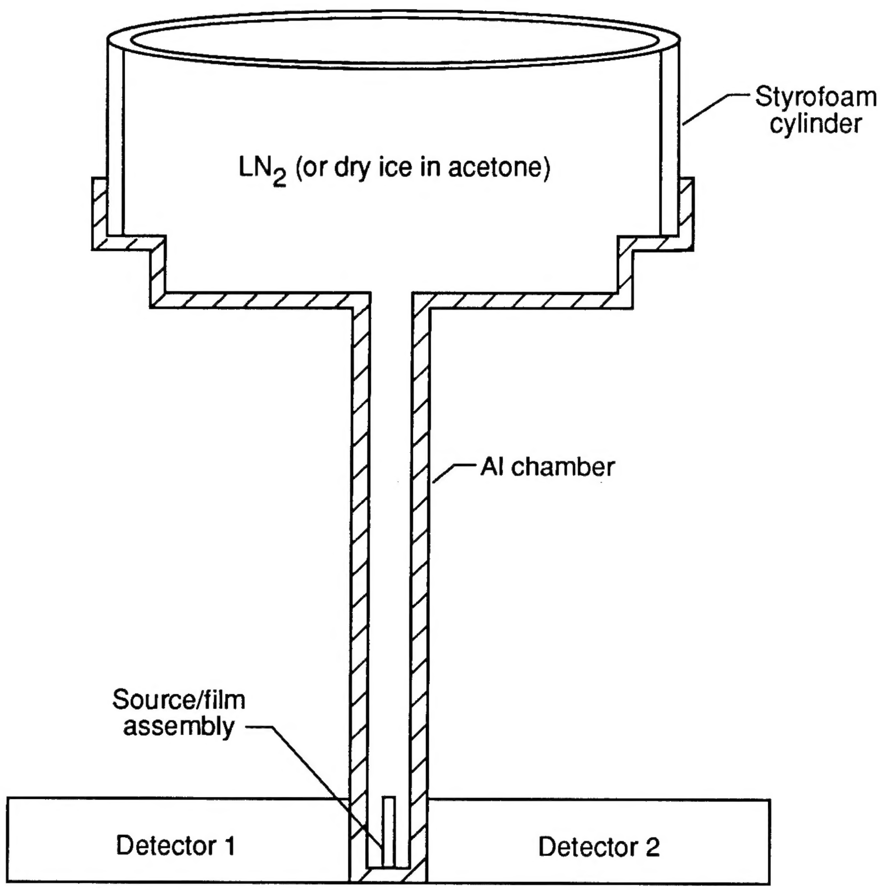

Figure 3. Schematic diagram of sample assembly for lifetime measurements at −62°C and −196°C.

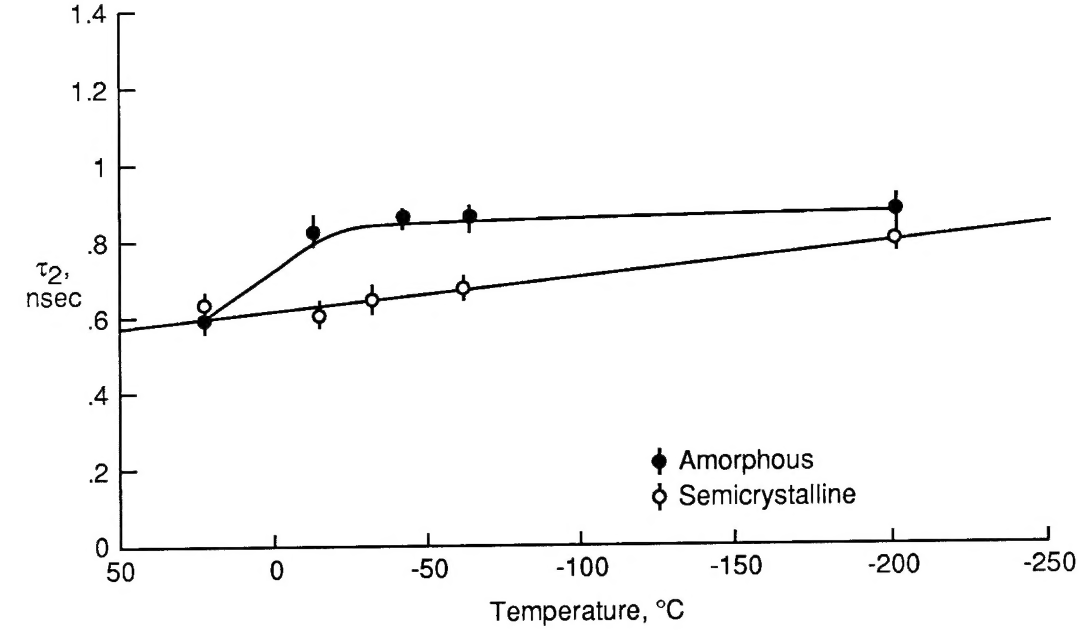

Figure 4. Second-component lifetime versus temperature in PEEK samples.

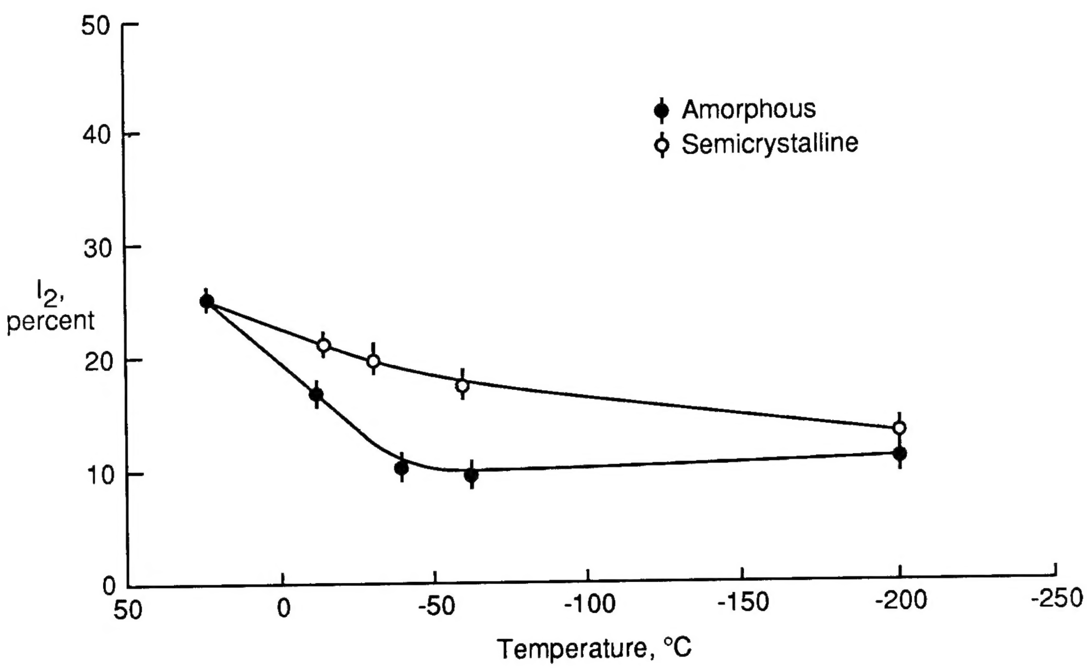

Figure 5. Second-component intensity versus temperature in PEEK samples.

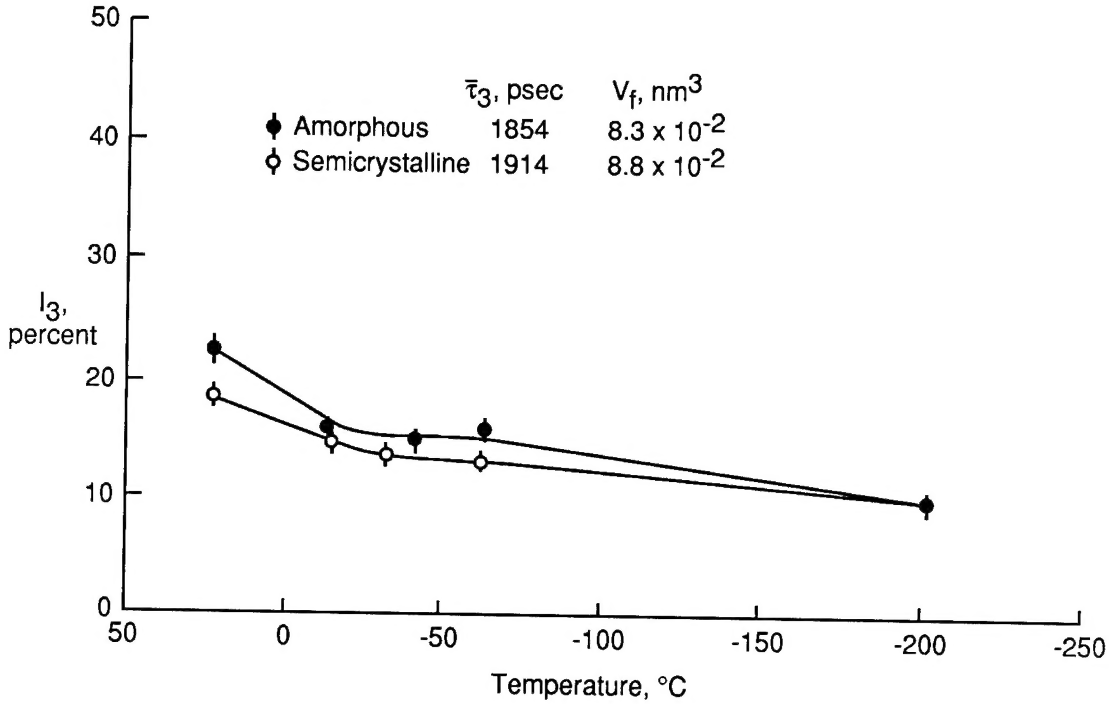

Figure 6. Third-component intensity versus temperature in PEEK samples.

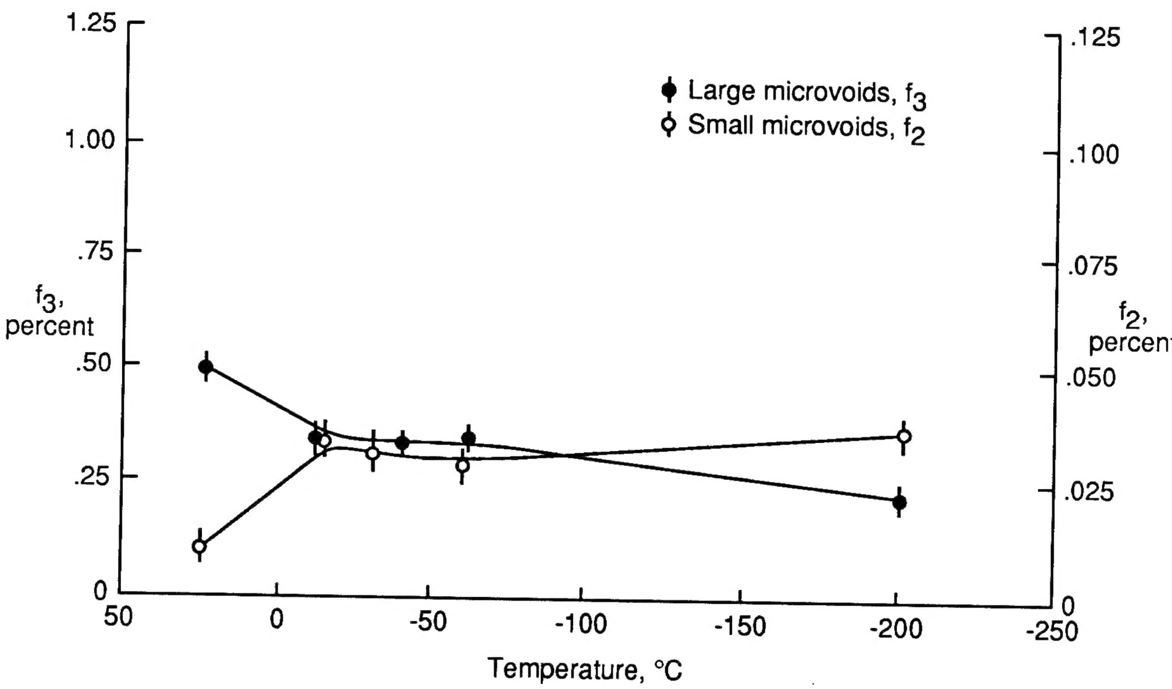

Figure 7. Microvoid fraction versus temperature in amorphous samples.

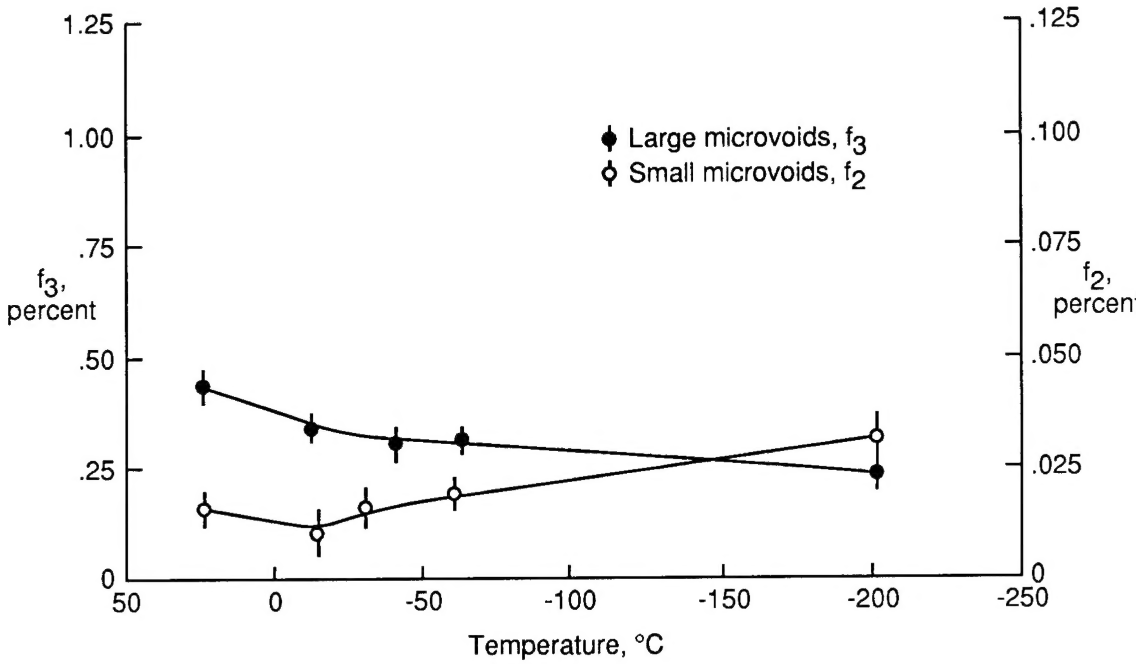

Figure 8. Microvoid fraction versus temperature in semicrystalline samples.

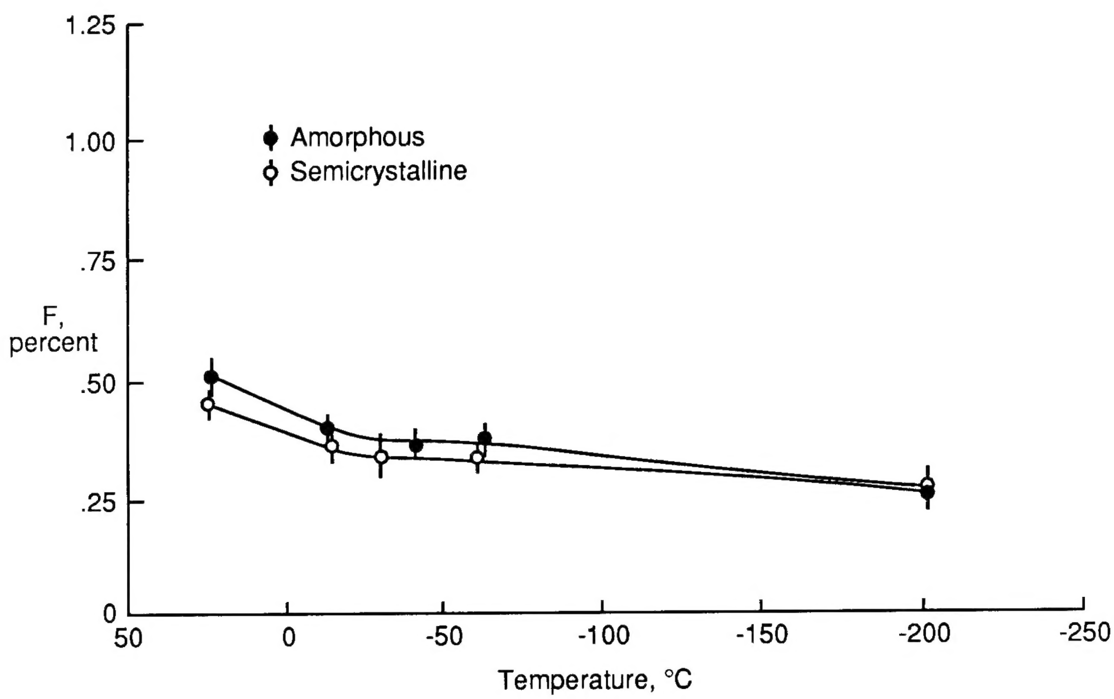

Figure 9. Total free-volume fraction versus temperature in PEEK samples.

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Report Documentation Page

1. Report No. NASA TP-3064	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Investigation of Microstructural Changes in Polyetherether-Ketone Films at Cryogenic Temperatures by Positron Lifetime Spectroscopy		5. Report Date March 1991
		6. Performing Organization Code
7. Author(s) Jag J. Singh, Abe Eftekhari, Terry L. St. Clair, and Danny R. Sprinkle		8. Performing Organization Report No. L-16841
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665-5225		10. Work Unit No. 506-43-21-05
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546-0001		13. Type of Report and Period Covered Technical Paper
		14. Sponsoring Agency Code

15. Supplementary Notes

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16. Abstract

Microstructural changes in polyetherether-ketone (PEEK) films have been investigated in the temperature range of 23°C to −196°C by using positron lifetime spectroscopy. It has been determined that the total free volume decreases by about 46 percent in amorphous PEEK samples and about 36 percent in semicrystalline PEEK samples when they are cooled from room temperature to the temperature of liquid nitrogen. If this trend in reduction of free volume with decreasing temperature continues, as expected, PEEK should be able to withstand cooling to the temperature of liquid hydrogen without any detrimental effect on its diffusivity for liquid hydrogen.

17. Key Words (Suggested by Author(s)) Polyetherether-ketone (PEEK); Cryogenic temperatures; Microstructural changes; Positron lifetime spectroscopy; Free-volume fraction; Liquid hydrogen diffusion	18. Distribution Statement Unclassified—Unlimited. Subject Category 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	12	A02

NASA FORM 1626 OCT 86

NASA-Langley, 1991